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One of the great challenges of inertial confinement fusion experiments is poor understanding of the effects of reactant heterogeneity on fusion reactions. The Marble campaign, conceived at Los Alamos National Laboratory, aims to gather new insights into this issue by utilizing target capsules containing polymer foams of variable pore size, tunable over an order of magnitude. Here we describe recent and ongoing progress in the development of CH and CH/CD polymer foams in support of Marble. Hierarchical and tunable pore sizes have been achieved by utilizing a sacrificial porogen template within an open-celled poly(divinylbenzene) or poly(divinylbenzene-*co*-styrene) aerogel matrix, resulting in low-density foams (*ca*. 30 mg/mL) with continuous multimodal pore networks.

KEYWORDS: low-density polymer foam, divinylbenzene, hierarchical porosity, sacrificial porogen

I. INTRODUCTION

Polymer foams are an important component of inertial confinement fusion (ICF) and other high energy density physics (HEDP) target designs. These targets are typically fielded at laser facilities such as OMEGA and the National Ignition Facility (NIF). Typical polymer foams appropriate for ICF targets include foams of polystyrene (PS) produced from thermally induced phase separation (TIPS) processes,[1] highly crosslinked PS from water-in-oil emulsions[2,3,4] or divinylbenzene (DVB) aerogels.[5,6] Where deuterium is required as a fusion reactant, deuterated polymers or monomers have been substituted for the H containing materials.[7,8,9] Often, open celled porosity is required in order to allow the introduction of fuel gases (deuterium, deuterium-tritium) into the porous network.

Use of particles as sacrificial porogen templates is an oft-employed route to porous materials.[10] In general the process involves forming an aggregate of the particle template; the interstitial spaces between particles are then filled with the desired material or material precursor; finally, the porogen particles are removed through pyrolysis or chemical leaching (see Figure 1). Thus, the final material contains voids where the particles had been, with uniformity dictated solely by the polydispersity of the particles. When the starting templates are colloidal crystals (crystalline 3D lattices of highly monodisperse particles) the resulting open celled porous materials are called inverse opals.[11] These materials find use in an array of applications throughout optics, energy storage, and a host of other areas. Colloidal crystal particles have a maximum packing efficiency of roughly 74 volume %.[11] Thus, the density of resulting inverse opals is on the order of 26% of full density, provided the interstitial space is completely filled with solid

material. Brownian motion enables colloidal crystallization: the individual particles assemble in the lowest energy configuration, typically by sedimenting out of a colloidal dispersion over a moderate time scale, followed by evaporation of the solvent.[11] In order to form colloidal crystals, particles must be nearly monodisperse in size. Moreover, the phenomenon is limited to particles of about 50 nm to 2 μm in size, because this is the scale at which Brownian motion is operative. Larger particles such as those used in the work reported herein (10 – 100 μm) are not subject to Brownian motion and therefore behave like macroscopic particles.[12] However, large particles can still be sedimented from dispersions, though their packing is into glassy aggregates having no long-range order. These materials have a much lower maximum packing efficiency than colloidal crystals (up to a maximum of about 63 %); thus, synthesis of materials having prescribed density requires thorough characterization of packing efficiency.[12]

The overall density required for foams in ICF targets is typically on the order of 1 to 10% of full density (depending on the specific material chemistry and its application) and so we required a low-density foam to fill the interstitial space between our sacrificial template particles. An open celled matrix conveniently allows the etching and subsequent removal of particles from the composite material even in the case where individual particles are isolated from one another.

Emulsion and phase separation/ phase inversion processes relevant to polymer foams for ICF targets applications produce open celled foams having small pores (ca. 1 μm or smaller). Unfortunately, these processes are not suitable for the introduction of particulate porogen templates. For high-internal phase emulsions, the precursor emulsion is too viscous to efficiently incorporate larger particles (>10 μm) into the host matrix with

uniform packing. For phase separating systems, the sequential de-mixing and freezing of constituent phases can be disrupted by the presence of a particle network, producing foams that are structurally anisotropic. Alternatively, DVB aerogel is an ideal material for this templating process. The precursor solvent, dibutyl phthalate, is moderately viscous, which serves to slow the sedimentation of particles enough to allow for better packing. Thus, silica microspheres or micro balloons can be dispersed in a DVB polymer precursor matrix, allowed to separate, the matrix polymerized, then the particles chemically leached out. At last the polymer gel is supercritically dried, resulting in the final product: open celled, hierarchically porous foam, the large pores being interconnected by the microporous polymer aerogel matrix (Figure 2).

II. EXPERIMENTAL

All chemicals were used as received with the exception of DVB/styrene monomers, and azobisisobutyronitrile (AIBN). Monomers were passed through an alumina column in order to remove polymerization inhibitors; AIBN was recrystallized from methanol.

Divinylbenzene Aerogel Foams. DVB aerogel of stoichiometry CH was produced as follows: for "smooth" foams having no large porosity, 30 mg/mL of DVB (Sigma-Aldrich, 80% technical grade) was dissolved in dibutyl phthalate (Acros Organics) along with 0.5 wt% of AIBN (Sigma Aldrich) in a sealed vial and heated to approximately 65 °C overnight. The resulting gel was solvent exchanged over several days to isopropanol (IPA, Fisher Scientific). The isopropanol gels were then supercritically dried as follows: gels were placed in a critical point drier (Quorum Technologies, Ltd., West Sussex, UK) and covered with additional isopropanol. The chamber was sealed and then filled with liquid carbon dioxide (10 °C, 51 atm). Over 24 h, alcohol was periodically drained from

the bottom of the vessel while replacing CO_2 and maintaining pressure. After the isopropanol had been completely exchanged for CO_2, the vessel was heated to 40 °C. During heating, pressure was increased and then maintained at 90 atm by periodically releasing CO_2. Upon reaching 40 °C, the vessel was slowly depressurized (greater than 1 hour) while maintaining temperature.

DVB aerogels having stoichiometry $CH_{0.5}D_{0.5}$ were produced in a similar manner, except using a 50/50 mixture of styrene d-8 (Cambridge Isotope, Inc.) and DVB in dibutyl phthalate. Attempts to increase the styrene d-8 to DVB ratio resulted in shrinking or collapsing of the resultant materials.

"Engineered" foams having large pores were prepared in the same way as smooth foams, except that porogens were introduced (silica microbeads of 10 μm diameter, or microballoons of 30, 50, or 100 μm diameter), and foams were prepared at a higher concentration (~60 mg/ mL), in order to provide a bulk density of ~ 30 mg/mL after leaching of the porogen template (packing efficiency in this system is 50%).

Introduction and Etching of Porogen. Silica beads or microballoons (Cospheric, Santa Barbara, CA) were added to gel precursor mixtures (60 mg/mL in dibutyl phthalate) and thoroughly mixed by sonication or vortex mixing. To promote packing, they were centrifuged at 2500 rpm for 20 minutes. After separation (sedimentation or creaming, depending on the density of particles used) samples were placed in an oven (65 °C) overnight to polymerize. After polymerization, composite gels were solvent exchanged several times over days for isopropanol in order to remove dibutyl phthalate. The gels were next exchanged for a 50% water/ alcohol mixture and then placed in a Teflon beaker with a 50% mixture of aqueous hydrofluoric acid (Sigma-Aldrich, 48%) in

6

isopropanol. The gels were allowed to soak for 48 hours before washing several times with 50/50 water/ isopropanol. The gels were finally exchanged for pure isopropanol before supercritical drying. Foams were characterized by optical and scanning electron microscopy (SEM); bulk density was determined by measuring the mass of a cylindrical specimen of known volume. Full removal of silica template and byproducts was confirmed by elemental analysis using energy dispersive spectroscopy (EDAX), integrated with our SEM instrument. Neither Si nor F was detected in the foams.

III. RESULTS

Initial experiments utilizing soda lime silica micro beads suffered from one main difficulty. Leaching in HF/ IPA over 72h or longer, at room temperature, was insufficient to fully remove the template. As a result we next substituted borosilicate silica micro balloons in place of solid beads (except in the case of 10 μm beads), our reasoning twofold: first, less total silica to be leached requires less HF; second, once the HF has penetrated the shell surface, dissolution can proceed from both the inner and outer balloon surfaces making the process much faster. Using the balloons did permit complete removal of the template over 48h. This substitution required a slight change to the overall process. The hollow micro balloons are buoyant in the dibutyl phthalate matrix and so they "cream" to the top surface rather than sedimenting to the bottom.

We found the packing efficiency of our template material to be consistent, at about 50% (determined by measuring bulk density), across all particle sizes. Therefore, we prepared the matrix polymer at double our desired final density.

CH DVB polymer foams (and CH/CD polymer foams) having bulk density of 30 mg/mL were successfully produced having large pores of 10, 30, 50, and 100 μm. Optical and

electron microscopy revealed a nearly homogeneous dispersion of large pores, though disordered (Figure 3). The DVB aerogel matrix showed its usual sub-micrometer porosity; moreover, there was no apparent change to pore morphology at the interfaces of the large porogen-templated voids (Fig. 2, right inset).
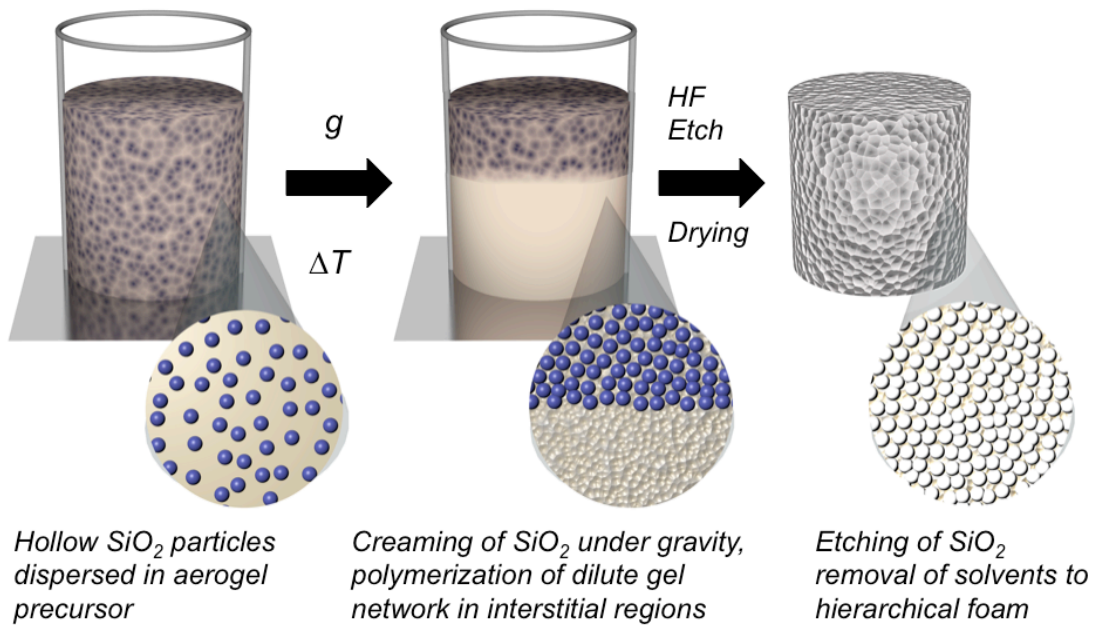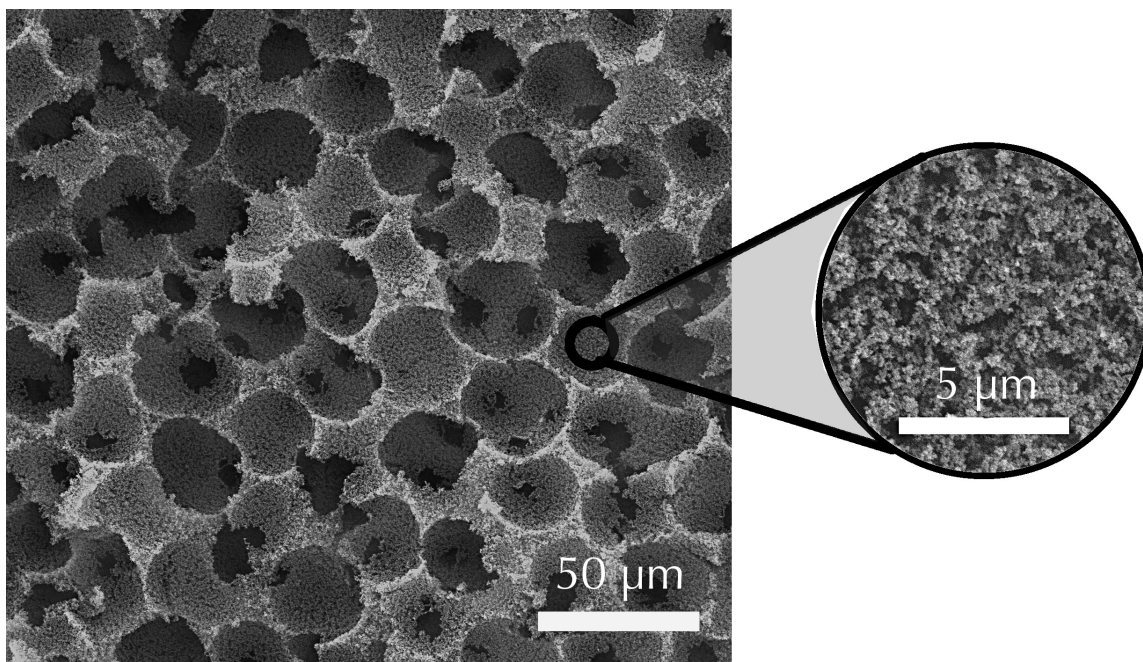
IV. CONCLUSIONS

We have successfully produced hierarchically porous DVB polymer aerogels utilizing a particulate porogen template process and supercritical drying. These materials have bulk density of 30 mg/ mL and stoichiometry of either CH or $CH_{0.5}D_{0.5}$. Matrix pore size is on the nanometer scale while the templated macropores were selected from between 10 and 100 μm in diameter. We are now investigating materials templated from mixtures of multiple particle sizes, and we are pursuing the synthesis of similar foams of CD stoichiometry.

Hollow SiO$_2$ particles dispersed in aerogel precursor

Creaming of SiO$_2$ under gravity, polymerization of dilute gel network in interstitial regions

Etching of SiO$_2$ removal of solvents to hierarchical foam

50 μm

5 μm
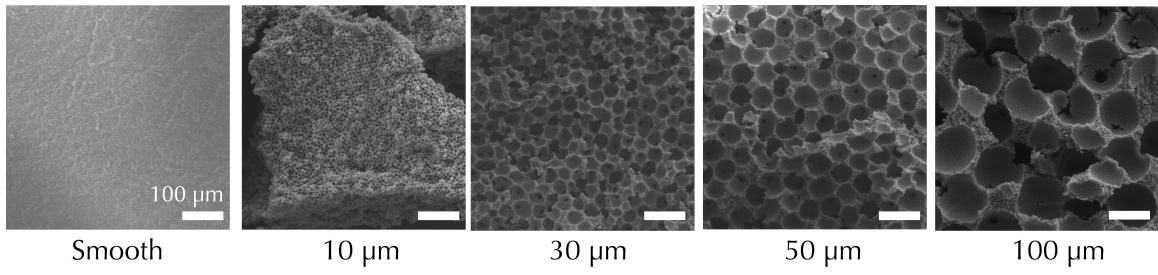
| Smooth | 10 μm | 30 μm | 50 μm | 100 μm |

Figure 1. Scheme for forming particle templated porous materials.

Figure 2. SEM image of hierarchical DVB foam.

Figure 3. SEM images of DVB foams, 10 – 100 μm pores. All scale bars 100 μm.

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